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Convenient preparation of fatty ester cyclic carbonates*

The cyclic carbonate moiety finds many industrial applications because of its unique chemistry and properties. Phosgene, a highly toxic and corrosive reagent, has been utilized in the past to prepare low yields of fatty ester compounds (**1**) that contain a five-membered cyclic carbonate group. Herein, we show $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$, tetramethylammonium hydrogen carbonate (TMAHC), to react efficiently with methyl or 2-ethylhexyl 9(10)chloro-10(9)-hydroxyoctadecanoate at 50–55 °C to give methyl or 2-ethylhexyl 8-(2-oxo-5-octyl-1,3-dioxolan-4-yl)octanoate, **1a** and **1b**, respectively. These fatty acid ester carbonates were isolated in good yields ranging from 84% to 91% after purification by vacuum distillation. The purified fatty ester carbonate compounds were characterized by ^1H and ^{13}C nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, and gas chromatography-mass spectrometry using electron impact ionization and positive chemical ionization techniques. This work demonstrates that the five-membered cyclic carbonate ring can be effectively introduced onto the alkyl chains of fatty acid esters using fatty ester chlorohydrins and $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$ chemistry. The well-known lubricating and polymeric properties of the carbonate moiety make these interesting cyclic oleochemical carbonates potential candidates for industrial lubricant, plasticizer, or polymer applications.

Keywords: Cyclic carbonates, 2-oxo-1,3-dioxolanes, chlorohydrins, tetramethylammonium hydrogen carbonate, oleic acid esters, nuclear magnetic resonance, mass spectrometry.

1 Introduction

Renewed interest in the use of fats and oils for sustainable chemistry has led to the growing importance of linear dialkyl carbonates (ROCOOR) [1], prepared from animal- and plant-based long-chain alcohols, and are currently finding use as components in lubricants [2], cosmetics [3], and plasticizers [4]. In contrast, only two reports describe the preparation of fatty ester carbonate compounds (**1**; Tab. 1) that contain a five-membered cyclic carbonate group as part of the alkyl chain [5, 6]. In these reports, phosgene, a highly toxic and corrosive reagent, is reacted with fatty ester vicinal diols to give low or unreported yields of cyclic carbonate compounds. Because of phosgene's toxicity and the importance of the cyclic carbonate moiety [7], alternative methods to prepare cyclic carbonates are being sought [8]. Carbon dioxide, a low-cost renewable resource, represents an attractive reagent for cyclic carbonate preparation, but is limited by its low reactivity. More recently, alkylammonium hydrogen carbonate reagents

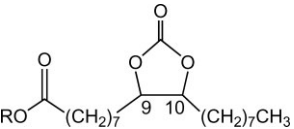
have been shown to react with short-chain disubstituted halohydrins such as $\text{R}_1\text{CH}(\text{OH})\text{CH}(\text{Cl})\text{R}_2$ ($\text{R}_1 = \text{CH}_3$ or Ph; $\text{R}_2 = \text{H}$, CH_3 or Ph) at 20 °C to give the corresponding disubstituted cyclic carbonates [9].

The application of alkylammonium hydrogen carbonate reagents to fatty acid chlorohydrin substrates has not previously been demonstrated. Herein, we show $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$ to react efficiently with methyl or 2-ethylhexyl 9(10)chloro-10(9)-hydroxyoctadecanoate at 50–55 °C to give fatty cyclic carbonates **1a** and **1b**, respectively, in 84–90% purified yields (Tab. 1). Characterization of the carbonates by ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), as well as electron impact ionization (EI) and positive chemical ionization (CI) gas chromatography-mass spectrometry (GC/MS) gives analytical data not previously reported in the literature.

* Disclaimer: Product names are necessary to report factually on available data; however, mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

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Table 1. Reaction parameters, yields, and physical properties of fatty acid ester cyclic carbonates (**1**) prepared from fatty acid ester chlorohydrins and $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$.

	Reaction time	Reaction temp. [°C]	Isolated Yield [%]	m. p. [°C]	b. p. [†] [°C]	Refractive Index [$n_D^{20.5}$]
1a	2.5 h	55	84.6	16.0–17.5	180 ¹⁴⁰	1.4592 ^{20.5}
1b	5.5 h	50	90.7	–44	185–190 ⁸⁵	1.4612 ^{20.5}

[†] Superscript denotes pressure in m Torr.

2 Materials and methods

¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker ARX 400 spectrometer (Billerica, MA, USA) with a 5-mm dual proton/carbon probe (400 MHz, ¹H; 100.61 MHz, ¹³C). FTIR spectra were obtained as films (NaCl), using a Perkin Elmer Spectrum RX FT-IR (Norwalk, CT, USA). GC was performed using a Hewlett-Packard (HP) 5890 Series II GC (Palo Alto, CA, USA) equipped with a flame ionization detector (280 °C) and a 30 m × 0.25 mm i.d. HP-5MS capillary column operating at 1.0 mL/min He flow at 15 psi (776 torr) head pressure; oven temperature ramp: 140 °C, for 2 min, ramp 140–280 °C at 20 °C/min, hold 30 min at 280 °C. GC/MS analyses were conducted using an HP 5890 Series II Plus GC coupled with an HP 5989B MS (Palo Alto, CA, USA). EI was performed at 70 eV. CI utilized methane reagent gas. The HP-5MS column (oven ramp as above) operated at 3 psi (155 torr) He head pressure; injector temperature, 250 °C; transfer line temperature, 280 °C.

2.1 General procedure for fatty cyclic carbonate (**1**) preparation

Gaseous CO₂ was bubbled through a stirred $(\text{CH}_3)_4\text{N}^+\text{OH}$ solution (25%, 8.45 g, 23.2 mmol) in MeOH (13 mL) at 22 °C for 1.5 h. The MeOH was removed *in vacuo*, MeCN (45 mL) was added, and the resulting $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$ suspension was stirred for 20 min under CO₂. A MeCN (5 mL) solution of methyl 9(10)chloro-10(9)-hydroxyoctadecanoate (5.34 g, 14.9 mmol) was added, and the stirred mixture was heated for 2.5 h at 55 °C under a CO₂ atmosphere. The resulting solid is filtered and washed with MeCN (2 × 30 mL). The combined MeCN washings are concentrated *in vacuo*, acetone (60 mL) is added to the residue, and the precipitated solid is filtered and washed with additional acetone (3 × 25 mL). The combined acetone solution is eluted through a short silica column (5 g) and concentrated to give a crude oil (4.74 g). Vacuum distillation (180 °C/140 mTorr) gave **1a** (4.49 g, 84.6%) as a white solid.

Methyl 8-(2-oxo-5-octyl-1,3-dioxolan-4-yl)octanoate (**1a**): ¹H NMR: δ 4.59 (*bddd*, 2H, J = 7.4 Hz), 3.63 (*s*, 3H), 2.27 (*t*, 2H, J = 7.5 Hz), 1.75–1.15 (*m*, 26H), 0.84 (*t*, 3H, J = 6.9 Hz). ¹³C NMR: δ 174.24, 154.82, 80.02, 79.98, 51.50, 34.04, 31.85, 29.38, 29.30, 29.19, 29.07, 29.04, 28.99, 28.95, 28.92, 25.66, 25.60, 24.87, 22.68, 14.13. IR (NaCl) cm⁻¹: 2928, 2856, 1801, 1739, 1465, 1437, 1367, 1174, 1089, 1042. MS (EI): *m/z* 357 (MH⁺, 2%), 325 ([M – CH₃O]⁺, 15%), 294 ([M – H₂CO₃]⁺, 8%), 262 (15%), 239 (34%), 55 (100%). MS (CI): *m/z* 397 ([M + C₃H₅]⁺, 7%), 385 ([M + C₂H₅]⁺, 22%), 357 (MH⁺, 77%), 325 ([M – OCH₃]⁺, 100%), 295 ([M – HCO₃]⁺, 5%), 281 ([M – CO₂]⁺, 12%), 263 (4%), 239 (2%).

2-Ethylhexyl 8-(2-oxo-5-octyl-1,3-dioxolan-4-yl)octanoate (**1b**): ¹H NMR: δ 4.60 (*bddd*, 2H, J = 7.1 Hz), 3.96 (*d*, 2H, J = 5.8 Hz), 2.28 (*t*, 2H, J = 7.5 Hz), 1.85–1.15 (*m*, 35H), 0.87 (*m*, 9H). ¹³C NMR: δ 174.06, 154.83, 80.02, 79.98, 66.76, 38.82, 34.41, 31.86, 30.49, 29.39, 29.32, 29.22, 29.14, 29.10, 29.05, 28.99, 28.97, 28.96, 25.68, 25.64, 24.99, 23.87, 23.04, 22.70, 14.15, 14.12, 11.06. IR (NaCl) cm⁻¹: 2956, 2928, 2857, 1805, 1735, 1465, 1377, 1176, 1043. MS (EI): *m/z* 455 (MH⁺, 0.2%), 392 ([M – H₂CO₃]⁺, 1%), 343 ([C₁₉H₃₃O₅ + 2H]⁺, 3%), 325 ([M – C₈H₁₇O]⁺, 100%), 280 (10%), 262 (6%), 239 (12%). MS (CI): *m/z* 483 ([M + C₂H₅]⁺, 8%), 455 (MH⁺, 64%), 411 ([MH – CO₂]⁺, 2%), 383 (C₂₂H₃₉O₅⁺, 4%), 371 ([C₂₁H₃₇O₅ + 2H]⁺, 14%), 343 ([C₁₉H₃₃O₅ + 2H]⁺, 18%), 325 ([M – C₈H₁₇O]⁺, 100%), 281, (18%).

3 Results and discussion

Tab. 1 gives reaction conditions for the preparation of (**1**) from methyl or 2-ethylhexyl 9(10)chloro-10(9)-hydroxyoctadecanoate. The $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$ reagent is simply prepared by saturating a stirred methanol solution of commercially available $(\text{CH}_3)_4\text{N}^+\text{OH}$ with CO_{2(g)} [9]. Reaction of the chlorohydrins with a slight excess of $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$ under a CO_{2(g)} atmosphere in MeCN at 50–55 °C gives cyclic carbonates **1**. Vacuum distillation

provides good yields of neat carbonate materials, for which some physical properties are reported (Tab. 1). Carbonate **1a** melts at 16.0–17.5 °C, and as can be seen, replacement of the methyl alcohol portion of the ester with the branched 2-ethylhexyl moiety (**1b**) caused a dramatic melting point decrease to –44 °C.

The main feature of interest in the ^1H NMR spectra of **1a** and **1b** are the carbonate ring hydrogen signals at 4.59 ppm. In the ^{13}C NMR spectra of **1a** and **1b**, the carbonate carbons at 154.8 ppm are considerably upfield to the ester carbonyl carbons at 174.2 ppm, and have similar chemical shifts to those for long-chain dialkyl carbonates [1]. The C9 and C10 carbonate ring carbons are at 80.02 ppm and 79.98 ppm, while the C-8 and C-11 carbon atoms flanking the carbonate ring have chemical shifts of approximately 25.6 ppm. The remaining hydrogen and carbon signals show chemical shifts typical of fatty esters. Electron impact (EI) and methane positive chemical ionization (CI) GC/MS confirmed the structures of **1a** and **1b**. Loss of HCO_3 or CO_2 from **1a** and **1b** molecular ions is characteristic of cyclic carbonate compounds, previously noted for low-molecular weight cyclic carbonates [10].

The results presented here establish that five-membered cyclic carbonate rings can be effectively introduced onto alkyl chains of fatty acid esters under mild conditions from fatty ester chlorohydrins utilizing $(\text{CH}_3)_4\text{N}^+\text{HCO}_3^-$. This chemistry avoids the hazards associated with phosgene use. These carbonate compounds are expected to have interesting chemistry and properties that make them candidates for lubricant, plasticizer, or polymer applications.

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